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Low Melting Nematic Derivatives of Phenyl 3-Methyl-Benzoyloxybenzoate

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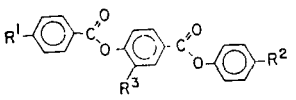
During recents months, several research groups have focussed their attention on the synthesis of novel derivatives of phenyl 4-benzoyloxybenzoate (1) in an effort to prepare stable nematic liquid crystals for physical, chemical and technological applications. Investigations by Steinstraesser[1] and by Young, Haller and Green[2] have uncovered stable nematogens of type 2 and 3, respectively, which exhibit wide nematic ranges and melting points in the vicinity of 90°C. Van Meter and Klanderman,[3] through the use of laterally-placed chlorine substituents, have prepared nematic derivatives of *1* which melt as low as 39°C.



1 $R^1 = R^2 = R^3 = H$.
2 $R^3 = H$; R^1 and R^2 are various substituents.
3 $R^3 = CH_3$; R^1 and R^2 are ethoxy and *n*-butyl or *n*-butyl and ethoxy.
4 $R^3 = CH_3$; R^1 and R^2 are *n*-alkyls.
5 $R^3 = CH_3$; R^1 = 2-methylpentyloxy; R^2 = *n*-butyl.

In this communication, we wish to disclose a series of forty-eight low melting nematogenic dialkyl derivatives (Table 1) of type 4, one of which melts to the

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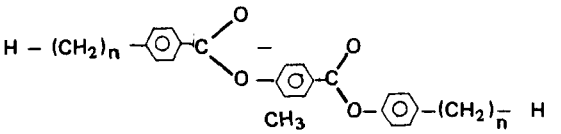
TABLE I

Nematic ranges (in °C) of some dialkyl derivatives of phenyl 4-benzoyloxy-3-methylbenzonate. The transition temperatures, determined on a polarizing microscope equipped with a Calibrated Mettler FP 2 Hot stage, are believed accurate to ± 0.5°C.

n \ n'	4	5	6	7	8	9
1	89–142	82–144	88–127	91–127	87–117	73–117
2	86–129	92–132	68–117	68–118	71–106	62–107
3	76–138	72–141	75–127	65–125	60–116	65–115
4	72–124	54–128	79–116	52–115	62–106	53–107
5	58–128	70–132	64–120	43–121	64–112	52–113
6	50–117	54–122	66–110	53–112	61–105	51–105
7	67–116	48–119	62–110	56–112	70–105	56–107
8	68–108	58–113	66–105	59–106	70–102	64–102



nematic phase at 43°C. These compounds were prepared by a novel, six-step procedure with an average yield per step of 90% (Figure 1). The benzyl group of intermediates **7–10** serves a dual function as a protecting moity; it enables the oxidation of acetophenone **7** to proceed cleanly, avoiding reaction failure which occurs with hydroxysubstituted acetophenones;[4] it allows the formation and

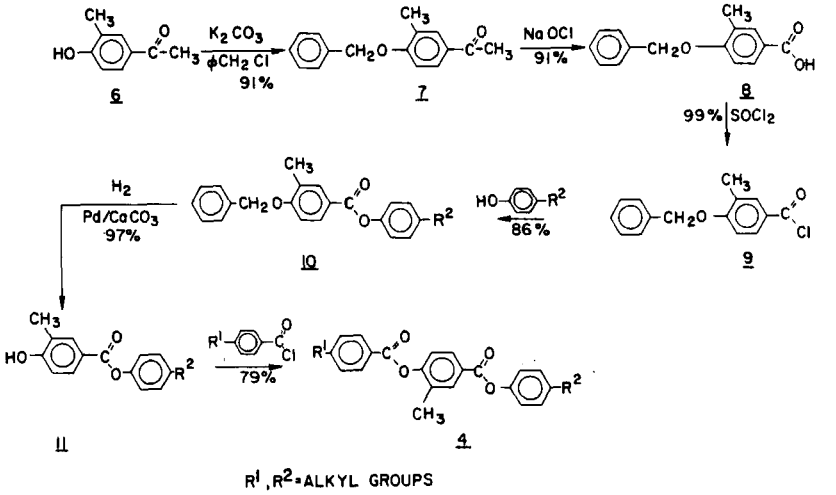


FIGURE 1 A new high-yield synthetic route to some ring-methylated derivates of phenyl 4-benzoyloxybenzoate.

simple esterification of acid chloride **9** without complication.

The stability of the diesters toward moisture, oxygen, and light is relatively high in comparison with the mesomorphic Schiff bases and chlorostilbenes.[2,5,6] For example, a ternary nematic mixture composed of equimolar quantities of **4** ($R^1 = C_7H_{15}$, $R^2 = C_4H_9$), **4** ($R^1 = C_5H_{11}$, $R^2 = C_4H_9$), and **5** (nematic range = 54–89°C) was sandwiched between a microscope slide and cover glass and was allowed to sit on the benchtop exposed to laboratory atmosphere and fluorescent lighting. After a six month period, the nematic-isotropic transition temperature of the mixture had dropped only 1°, from 111° to 110°C.

The diesters **4** are colorless, crystalline materials that exhibit broad nematic ranges. No smectic properties were observed, even in the higher homologs. For the investigation of their physical properties at room temperature, several mixtures of diesters were prepared; however, the tendency for these mixtures to remain in the supercooled state makes the determination of melting points difficult. Work is in progress at IBM laboratories on the preparation of mixtures with accurately known low melting points and on the study of their electrooptical properties.

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